DEVELOPMENT OF AN EXTRACTIVE REACTOR BLOCK IN THE ASPEN PLUS SIMULATOR

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Thesis submitted in partial fulfillment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
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JUNE 2012

ABSTRACT

The design and operation issues for extractive reactor system are considerably more complex than those involved for either conventional extraction column or convention reactors. The introduction of an in situ separation function within the reaction zone leads to complex interactions between liquid-liquid equilibrium, liquid-liquid mass transfer, intra-catalyst diffusion (for homogeneously catalysed processes) and chemical kinetics. The advantages of such alternatives is the use of simultaneous extraction and reaction to improve the yields and/or selectivity to the products, and also that they require smaller recycle flows. This research is to purpose a suitable configuration for extractive reaction by identify the important parameter that affect the process and develop the kinetic subroutine in Aspen Plus simulation. The reactor block is design by using the Aspen plus simulation to set up and specifies the application type. It is combining with an Excel spreadsheet to performance the calculations by using Dynamic Data Exchange (DDE). From the simulation, it show out that the production of for the first stream with 249.430 kmol/hr methanol, 687.099 kmol/hr fatty acid methyl ester, and 336.185 kmol/hr glycerol. However, for the second stream which produce 133.780 kmol/hr triglyceride, 137.452 kmol/hr methanol and 118.889 kmol/hr fatty acid methyl ester. For the reactor block design it is an integrate current, future technology in exciting plant and also perform plant optimization and control to improve the plant competitiveness.

Keywords: Simulation, Methanol, Triglyceride, Extraction, Kinetics, reactor

ABSTRAK

Isu-isu tentang reka bentuk dan operasi untuk ekstraktif reaktor sistem adalah jauh lebih kompleks daripada yang terlibat sama ade konvensional pengekstrakan ruang ataupun konvensyen reaktor. Pengenalan mengenai satu in situ fungsi pengasingan dalam zon tindak balas membawa kepada interaksi kompleks antara cecair keseimbangan, pemindahan jisim cecair-cecair, pemangkin resapan dalaman (untuk pemangkin proses homogen) dan kinetik kimia. Kelebihan alternatif itu ialah penggunaan pengekstrakan dan reaksi serentak untuk meningkatkan hasil ataupun selektiviti untuk produk, dan juga bahawanya keperluan lebih kecil kitar semula aliran. Kajian ini adalah bertujuan untuk konfigurasi yang sesuai bagi tindak balas ekstraktif oleh mengenalpasti parameter penting yang mempengaruhi process dan membangunkan subrutin kinetic di Aspen Plus Simulasi. Blok reaktor adalah direkabentuk dengan mengunnakan Aspen Plus Simulasi untuk menubuhkan dan menentukan jenis aplikasi. Ia menggabungkan spreadsheet Excel untuk melaksanakan pengiraan dengan menggunakan Dynamic Data Exchanger (DDE). Daripada simulasi, ia menunjukan bahawa pengeluaran untuk aliran pertama dengan 249.430 kmol/hr methanol, 687.099 kmol/hr lemak asid metil ester dan 336.185 kmol/hr gliserol. Walau bagaimanapun, bagi aliran kedua yang menghasilkan 133.780 kmol/hr trigliserida, 137.452 kmol/hr methanol dan 118.889 kmol/hr asid lemak metil ester. Bagi reka bentuk blok reaktor ia adalah mengintegrasikan semasa, teknologi masa depan dalam penumbuhan yang menarik dan juga melaksanakan pengoptimimuman loji dan kawalan untuk meningkatkan daya asing sesebuah kilang.

Kata kunci: Simulasi, Methanol, Trigliserida, Pengekstrakan, Kinetik, Reaktor

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

T	Temperature
m_L	Mass of lemongrass
t	Time
C_O	Initial concentration
E	Usage of solvent
V	Volume of extract
V_O	Volume of oil
m_O	Mass of oil
α	Distribution coefficient

LIST OF ABBREVIATIONS

Mol/mol	Mole per mole
v/v	Volume per volume
CO_2	Carbon dioxide
Conc.	Concentration
Ed.	Edition
vol.	Volume

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

In recent years, process integration seems to be more important for the industry plant design process. It is related to all operations that involved in the production of one specific product. This can be achieved through the development of integrated processes that combine different steps into one single unit. Generally it is more common research in the biphasic reaction for a multifunctional reactor. The development of reactive separation process as alternatives to the conventional process has been actively pursued. Sánchez O. J. justified that the reactive extraction is an integrated process simultaneously combining the chemical reaction and the liquid-liquid extraction. By combining reactions with a liquid-liquid phase separation significantly it will improve in yield and selectivity of desired products and ease of separation of byproducts can be obtained. The latter phenomenon allows the continuous removal of the reaction products favoring the direct conversion in the case of reversible reactions like the esterification of vegetable oils with methanol.

The biodiesel is a mixture of methyl or ethyl esters of fatty acids that can be used as a fuel for diesel engines. It has good potential as an alternative diesel fuel not only because of environmental benefits but also because of being a renewable substitute of fossil fuel. Biodiesel can also be used as an environmentally friendly solvent or lubricant. The ester group increases the oxygen content of diesel-biodiesel blends improving the efficiency of the combustion of the conventional fossil diesel. For producing biodiesel,

the transesterification of vegetable oils with low molecular weight alcohols like methanol or ethanol is necessary (Gutiérrez L. F., Sánchez O. J. and Cardona C. A., 2010).

Usually, biodiesel production in the world is carried out employing methanol and basic catalysts (mostly KOH). The most employed vegetable oils are rapeseed, soybean and sunflower oils. The oil from palm (*Elaeis guineensis*) is considered as an excellent feedstock for biodiesel production in tropical countries (Gutiérrez L. F., Sánchez O. J. and Cardona C. A., 2010).

The conventional technologies for biodiesel production employ reactors with acid or basic catalysts and a separation scheme that uses unit operations like distillation, centrifugation, flash evaporation, filtration, and decantation. The purification of this biofuel through the operation mentioned implies high capital investment and energy consumption leading to elevated production costs. Process design trends in chemical industry are related to the development of more efficient technologies. One of the most important approaches for the design of more intensive and cost-effective process configurations is process integration, which looks for the integration of all operations involved in the production of one specific product. This can be achieved through the development of integrated processes that combine different steps into one single unit. The reactive extraction is an integrated process simultaneously combining the chemical reaction and liquid-liquid extraction. The latter phenomenon allows the continuous removal of the reaction products favouring the direct conversion in the case of reversible reactions like the esterification of vegetable oils with methanol. The objective of this work is to evaluate the possibility of applying the integration principle to the biodiesel production from palm oil by extractive reaction (Gutiérrez L. F. et. Al, 2010).

Methanol is commonly used in industry biodiesel production as a result of its relatively low cost and easy availability. As the non-catalytic transesterification is too slow and energetically unfavorable, acid or base catalysts are used. The classical reaction protocol for transesterification of triglycerides with methanol using homogeneous catalysts such as sodium methoxide requires mixing and stirring the reagent in the bath

reactor. At the end of the reaction, the non-polar phase containing the ester and the polar phase containing glycerol and methanol are separated to recover the products, catalyst, and the excess of methanol. After the ester is separated, other purification steps may be required, for example, washing, distillation, and/or extraction to remove remaining glycerol and other impurities. The excess of methanol recovered from the glycerol phase is usually reused, and the by-product glycerol can also be valorized to improved the economics of the process (Arumugam Sivasamy et. Al, 2009).

For scaling-up and optimizing the production of biodiesel, extractive reactor has a solid approach and compromise for the process. Furthermore, the combination of extraction and reaction offers a lower cost compared to the usage of each single extraction column and reactor as well.

1.2 PROBLEM STATEMENT

The need and demands for fuel has been rising for the past years as a result to increment price of world's crude oil. Fossil fuel that has been the major contributor to global economy is unsustainable but yet the demand for the energy is increasing year by year, as well as increases of environmental and human health impact. This contributes to the high productions of biodiesel fuel as an alternative fuel that costless and environmentally harmless. In other words, the combination of reaction and extraction within one unit operation is called reactive extraction which can contribute to costless operation while production these demands. The direct removal of the products or intermediates results in higher conversions and selectivity in comparison with the classical, sequential approach.

Since the extractive reaction is quite new in development, there is still under construction research for extractive reactor column. In order for extractive reactor to be used in the biodiesel plant, the feasibility and operating parameters need to be studied so that a suitable configuration can be posed to build the extractive reactor column. Soon, it will be one of the important simultaneous implementation of reaction separation within a

single unit of column. The natural multiple function of extractive reactor become more and more popular to be explored in several other chemical production and reactions.

A simulation must be carried out to predict the results and study the possibilities before a plant can be built for production purposes. Simulation is also useful for the preliminary design before a pilot plant is being built for experiment study. In this study, the performance of esterification of triglyceride and methanol catalyzed by sodium methoxide in the extractive reactor will be simulated by incorporating the thermodynamics model, kinetic model and the reactor model. Aspen-Plus simulator will be used as a tool for the simulation by incorporating the appropriate thermodynamics and kinetic models.

1.3 OBJECTIVES

The specific objectives of this study are:

i. To purpose a suitable configuration for extractive reaction
ii. To identify the important parameter that affect the process in extractive reactor
iii. To develop the kinetic subroutine in Aspen Plus simulation

1.4 SCOPE OF STUDY

In order to achieve the objectives of this project, the scopes of study are as below:

I. The reaction of palm oil transesterification to produce biodiesel by using methanol
II. Setup base case extractive reactor using existed reaction and using suitable thermodynamic properties and kinetic subroutine in the ASPEN Plus 12.1

1.5 RATIONAL AND SIGNIFICANT

Rationally, in this present study, simulation should be considered before setting up the biodiesel plant, this will cost of preventing from building not appropriate plant. The simulation study also can bring forward toward reducing the cost of building the plant. Significantly, the main purpose of this study can be achieved by finding the important parameters that can be cooperating into extractive reactor block before building up the plant to produce biodiesel.

CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL CONSIDERATION

Global competition among chemical companies has distributed to the industrial interest in cutting capital and operating costs. At the same time, as environmental regulations becomes increasingly stringent, the costs associated with waste management are expected to rise. Separation technologies could be improved in terms of energy efficiency, productivity or raw materials use by coupling it with chemical synthesis (reaction). At the same time, reaction system efficiency can be improved by coupling it with separation. The potential is greatest when both expect are important the combination has a potential for capital productivity improvements and selectivity improvements, reduced energy use and the reduction or elimination of solvents.

2.2 REACTOR OPTIMISATION

The reactive separation processes involve the integration of chemical reaction into another separation operation such as distillation, absorption, adsorption, extraction, membrane reactors, the reactive crystallization and reactive precipitation. The additional degrees of freedom in the unit design offer the possibility to tailor the concentration profiles inside the unit in order to achieve better process performance. Especially the in-situ separation results in continuous removal of product, which not only generally overcomes the limitation of chemical equilibrium but also suppresses the side reactions for many cases. (S.B. Gadewar et. Al. 2004).

2.2.1 Biphasic Reaction

The term of biphasic reaction can be defined as a reaction equipment in which performance is synergetically enhanced by means of integrating one or more additional process functions. The desired improvement can refer to the difference characteristics, such as yield and productivity; investment and operating costs or flexibility and safety in an industry. The other common principle involves a modification of the temperature or concentration profile in the reactor. The most general definition of a biphasic reaction embraces both state-of-the-art technologies.

The actual concept for the biphasic reaction is to analyse the reactor in terms of the type and direction of the predominant heat and mass transfer processes. By considering diffusive or convective transport mechanisms for heat or mass parallel or perpendicular to the flow direction with internal or external sources and sinks it proved possible to define sixteen distinct reactor permutations. Packing within the reactor was allowed to function as a catalyst, as an adsorbent and as a medium for regenerative heat storage (David W. Agar, 1999).

In principle, transesterification is a reversible reaction, although in the production of biodiesel, the back reaction does not occur or is negligible because the glycerol formed is not miscible with product, leading to a two-phase system. Nevertheless, an excess of alcohol is usually employed to force reaction towards the right side. Since the reaction is still involve in several mixing composition, hence the extraction process is needed to separate out the pure Methyl esters (biodiesel). The reactions for palm oil transesterification are shown:

$$\text{Triglyceride} + 3\ \text{Methanol} \leftrightarrow 3\ \text{FAME} + \text{Glycerol}$$

However, transesterification also correlated to the Le Chateliers principle. The reaction of palm oil transesterification is a reversible reaction, the reaction happen will always in the mixture form of product and reagent or material. Hence, Le Chateliers

Principle is able to predict the effect of a change in conditions on the transesterification of chemical equilibrium. The chemical system at equilibrium of exterification process will experiences a change in concentration, temperature, volume, or partial pressure; adding an inert gas and catalyst as well. Then the equilibrium shifts to counteract the imposed change and a new equilibrium is established. This principle is generally used in biodiesel production in order to manipulate the outcomes of reversible reaction, often to increase the yield of reaction. It will give a great equilibrium system shifts to the right to produce more final product – FAME.

Generally in some period study that, second-order kinetics has been observed at 6:1 methanol/oil molar ratio. Depending on the systems, second-order, pseudo-second order, or, at higher excess of MeOH, pseudo-first-order kinetic models have been successfully applied for data fitting. In most cases, Sivasamy (2009) claim that the observed reaction rates and calculated constants are indeed reflecting the chemical processes and not mass transfer processes. As the methyl ester is accumulated, it acts as a mutual solvent and ultimately a single-phase system is formed which is favourable for a kinetically controlled process. An accurate analysis of kinetic data on the transesterification process can be very helpful for the process optimization. The Reaction kinetic rate, $-r_A = k_1[C_{TG}{C_{Al}}^3 - \frac{{C_{FAME}}^3 C_{gly}}{Kc}]$.

2.2.2 Liquid-liquid extraction

Liquid extraction (or solvent extraction) refers to an operation in which the components of a liquid mixture are separated by contacting it with a suitable insoluble liquid solvent which preferentially dissolves one or more components. In this operation, the separation of the components depends upon the unequal distribution of the components between the immiscible liquids. The feed solution represents one phase and the solvent to be used to effect separation represents the second phase. The mass transfer of the solute liquid takes place from the feed solution to the solvent phase. Extraction is a separation process aiming to purify the feed or to recover one or more compounds from it (Claudia Irina Koncsag and Alina Barbulescu, 2007).

For the analysis purpose, the palm oil was considered to contain triolein, tripalmitin and trilinolein. Each fatty acid has a defined percentage content that characterizes the properties of palm oil. Each fatty acid has a defined percentage content that characterizes the properties of palm oil. The glycerol phase corresponds to the raffinate and the biodiesel (FAME) phase corresponds to the extract. In the transesterification process, in extraction column, the palm oil will be the feed that will react with methanol. Then, fatty acid methyl ester (FAME) and several methanol will be the extract solvent while glycerol and heavy phase methanol will be the bottom liquid product. Due to the pass study that, high-molecular-weight fatty acids of (FAME) can be separated from palm oils by extraction with liquid methanol or by high-vacuum distillation, which is more expensive. The distribution coefficients, $k = \frac{y_{e\,(methanol/glycerol)}}{x_{r\,(oil/\,FAME)}}$. The solvent extraction normally is $Y_e = \frac{C_{FAME}}{C_{FAME}+C_{methanol}+C_{glycerol}}$ and the rectifine is $X_f = \frac{C_{FAME}}{C_{FAME}C_{TG}}$.

2.2.3 Implementation of Extraction into the reaction

The application of extractive reaction is one of the integration approaches that can be utilized for the intensification of biodiesel production. This process consists in the combination of the chemical reaction and liquid-liquid extraction in the same unit achieving such synergistic effect, that the increase of selectivity, conversion, productivity, and purity of final product may be attained (Rivera and Cardona, 2004).

The solvent extraction is to removed FFA or triglycerides and treats separately with acid or base esterification. This will make it more coproducts from fatty acids and more coproducts from glycerin extract more trace compound. Since it is a reversible reaction, the equilibrium will not only shift to the left to produce more fatty acid but also will shift to left to reverse the reaction. So, the conversion of triglycerides which make up oils into fatty acid esters and glycerol will be increase by adding extraction in a reactor. In the extraction, the related mass transfer limitations usually significantly reduce the rate

and efficiency of the reaction. While for the reaction, high energy consumption and costly separation of the catalyst from reaction mixture have inspired the development of heterogeneous catalyst. Furthermore, solid acid catalysts can indeed improve the sustainability of the biodiesel production process. Notably, diffucional limitations might sometimes drastically reduce the surface of the solid that is available for promoting the transesterification reaction. Therefore, a design of the pore structure of these materials is important (Arumugam Sivasamy et. Al, 2009).

2.3 SIMULATION SOFTWARE

The purpose of analysis/ simulation is to model and predict the performance of a process. It involves the decomposition of the process into its constituent element (units) for individual study of performance. The process characteristics (flow rates, compositions, temperatures, pressures, equipment sizes, etc.) are predicted using analysis techniques. These techniques include mathematical model, empirical correlations and computer-aided process simulation tools (ASPEN Plus). In addition, process analysis may involve the use of experimental means to predict and validate performance. Therefore, in process simulation, we are given the process inputs and flow sheet and are required to predict process outputs (Fig. 2.1). The lab will focus on ASPEN Plus. It is a computer-aided software which uses the underlying physical relationships (eg., material and energy balances, thermodynamic equilibrium, rate equations) to predict process performance (e.g., stream properties, operating conditions, and equipment sizes).

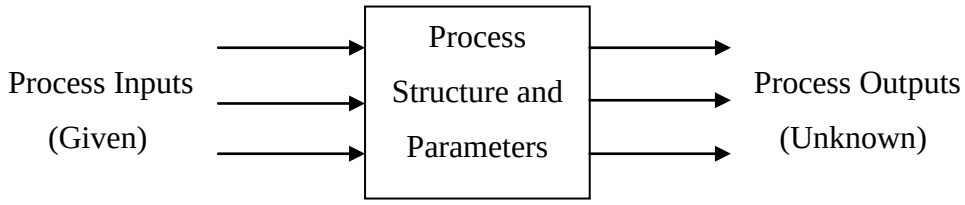

Figure 2.1: Process Simulation Problems

2.3.1 Subroutine-enabled block for customized unit

Subroutines help our programming for two main reasons. First, they let us reuse code. This makes it easier to find and fix bugs and makes it faster for us to write programs. The second reason is that they allow us to chuck our code into organizational sections. Each subroutine can, for example, be responsible for a particular task. It will show the structure of program easily.

The subroutine-enabled block is an additional info or software that adds into the ASPEN Plus. There might be certain term of reaction or mathematical modelling equation that cannot found in ASPEN Plus, then it will need other software to do it. Normally, user subroutine is used to link it with ASPEN Plus for the further simulation progress. In here, the subroutine is needed to find out the kinetic reaction which is used in the reactor block. Hence, in order to successfully using this subroutine, the other connecting program is needed to match it into the aspen plus.

CHAPTER 3

METHODOLOGY

3.1 SIMULATION STEPS

In this research, there are a few steps to develop the extractive reactor block. In order to develop the reactor block, we need to identify the parameter that will be used in Aspen Plus User Interface. Microsoft Excel Solver will be used to solve the unknown in extraction process, and the suitable kinetic subroutine will be developed to find out the kinetic reaction of the process. Therefore, a final reaction rate for the extractive reactor bock will be achieve by using the result of parameter and equation from both extraction and reaction process. In here, Dynamic Data Exchange (DDE) is used link and connects it to Aspen Plus User Interface. Lastly, simulate the reactor block. The expected result and data will be directly come out. The data will be then validated with report data in literature review.

Aspen plus simulator is used to model and predict the performance of a process which involves the decomposition of the process into its constituent elements for individual study of performance. It is widely used to study and investigate the effect of various operating parameters on various reactions.

The Figure 3.1 below is the overall methodology flow chart of the development of extractive reactor block in the aspen plus simulation.

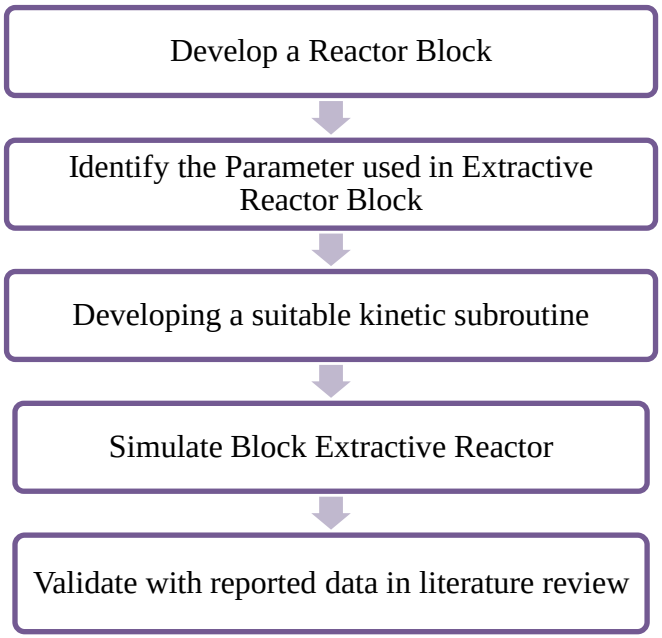

Figure 3.1: Overall Methodology Flow Chart

3.2 DEVELOPMENT OF REACTOR BLOCK

The extractive reactor simulation is used to simulate the reactor block and started with the creating an Excel unit Operation Model. The model in Aspen Plus is setting up and specifies the application type before run the aspen. In the Aspen Plus simulation it will combine with an Excel spreadsheet to performance the calculations.

The Aspen Plus is use to build a process flow sheet, specify feed and product streams, and enter the real and integer parameter corresponding to the model. Then use Excel to create a spreadsheet to calculate product stream properties. Aspen Plus will write data to and read data from the Excel spreadsheet.

3.2.1 Basis of Model Development

The development for extractive reactor block for the production of FAME is used as the basis of model development. It is based on the pervious analysis that the reaction inlet and outlet is satisfied based on the journal. Its configurations and specifications are shown in the following figure:

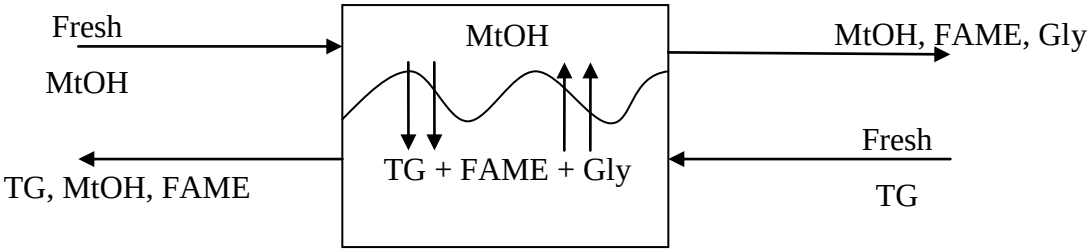

Figure 3.2: The Configurations and Specifications Used as Block Development Basis

3.2.2 Model Assumptions

The following assumptions are made for the extractive reactor block simulation:

1. There is only liquid fluid leaving a stage are in thermal equilibrium
2. Heat of mixing of liquid mixtures are negligible
3. Negligible vapour holdup on trays
4. Liquid on each stage is perfectly mixed
5. The block does not lose heat to the surroundings and is adiabatic

3.2.3 Simulation Extractive Reactor Block

The extractive reactor simulation is used to simulate the reactor block and started with the creating an Excel unit Operation Model. The model in Aspen Plus is setting up and specifies the application type before run the aspen. In the Aspen Plus simulation it will combine with an Excel spreadsheet to performance the calculations.

First use Aspen Plus to build a process flow sheet, specify feed and product streams, and enter the real and integer parameter corresponding to the model. Then use Excel to create a spreadsheet to calculate product stream properties. Aspen Plus will write data to and read data from the Excel spreadsheet.

3.2.3.1 Setting the Properties

Every part of the process flow sheet must be assigned a parameter property attribute. The property methods and model must be fix first before go to the forward steps. This is important to know that what situation is set for the Block to simulate. In the Aspen plus it is important to build the process flowsheet. It matters which stream was created first and will be passing Excel data to Aspen Plus array that contains product stream data. The first stream declared also come first in the data array.